Final Technical Report for:
'iffusion in Ordered and Disordered Media
N00014-90-J-1028

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S-11-92

ABSTRACT

In this project, we have investigated the Brownian motion taking place in ordered and disordered media using various complementary approaches. These include the analysis of the eigenvalues and eigenvectors of the transition probability matrix (which represents both the media geometry and the kinetics of Brownian motion). This matrix is typically a large, random, Markov matrix and is shown to possess eigenspectrum with scaling properties which has been analyzed numerically. Secondly, the same matrix has been used to evaluate autocorrelation functions directly and exactly taking advantage of high speed vector computation. Thirdly, the Langevin approach to diffusion has been extended to incorporate the *anomalous* diffusion on *fractal* media. Lastly, the frequency dependent conductivity of inhomogeneous media has been investigated using a *persistent* random walk model and the aforementioned numerical technique of the calculation of step autocorrelation functions. This last work has already revealed the unexpected effects of the interplay between the mean free path of the diffusing particle (*carrier*), the carrier density, and the length scale of inhomogeneity in the media. This work represents what we believe to be the coherent efforts to understand the diffusion and transport in disordered media.

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In the past 30 months, we have carried out a detailed study of the diffusive transport in ordered (but not uniform) and disordered media from a number of different perspectives. We have summarized below some of the results of this project. It is clear that we have only scratched the surface of this very important and complex problem in cluster science, and we hope to continue this research after the termination of the grant.

I. Eigenspectrum of Transition Probability Matrix

First, we have conducted a study of the eigenspectrum of the transition probability matrix W (which describes both the geometry of the medium and the particular kinetics of diffusion). In this project, we considered the discrete-time random walk on a cluster formed on a discrete lattice by randomly diluting the lattice with independent probability $1 - p$. The remaining sites (fraction p) then form connected components where the connectivity is defined by nearest neighbor bonds between remaining sites. These connected sets are simply the *percolation* clusters,[1] and we have studied the Markov matrix W which corresponds to the so-called *myopic* and *blind ant* random walks[2] on these clusters.[3-5]

On the one hand, the random walk confined to a critical percolation cluster (i.e., at $p = p_c$) is known to execute *anomalous diffusion*,[6] and on the other hand, if the disorder is weak (i.e., $p > p_c$), a *long time tail* appears, e.g., in the velocity autocorrelation function.[7,8] In the past, these different regimes were studied mostly separately (often by disjoint group of researchers) using rather different approaches. Our current study of the eigenspectrum of W puts the two regimes on the same footing and enables the discussion of the crossover between them from the unified point of view.

For example, the density of the eigenvalues $n(\lambda)$ can be shown to be essentially the inverse Laplace transform of the probability for the random walk to return to the starting point.[5,9] The latter scales as function of time as $t^{-x/2}$ where $x = d_s$ (the spectral dimension[10]) at $p = p_c$, while for $p > p_c$, the scaling exponent is $x = d$ (the spatial dimension). Thus we expect

$$n(\lambda) \sim |\ln \lambda|^{\frac{x}{2}-1} \ , \tag{1}$$

where the last exponent is about $-1/3$ in both two and three dimensions at p_c, crossing over to 0 and 1/2 for $p > p_c$ in two and three dimensions respectively. These scaling relations have indeed been confirmed and is illustrated in Fig.1. Similarly, the velocity autocorrelation function can be related to the Laplace transform of a function $\pi(\lambda)$ (related to $n(\lambda)$ and to the eigenvectors for λ), and thus the scaling exponent for the

long-time tails can be related to the behavior of $\pi(\lambda)$ as $|\lambda| \to 1$. Such scaling relations have also been numerically confirmed by our eigenspectrum analyses.[4,5]

II. Exact Enumeration of Autocorrelation Functions

Second, an exact enumeration approach[11,12] was used to study the various autocorrelation functions of the Brownian motion as well as other related problems. In this approach, all Brownian paths on a finite cluster are summed exactly by simply multiplying the matrix W repeatedly to the appropriate initial state (which is constructed from the initial probability distribution for the position of the random walker and the quantity of interest to calculate). Clearly, this method is ideally suited to the high speed vector computations, allowing the calculation of autocorrelations easily for 10^5 time steps or more. Such calculations were performed to show and analyze the persistent oscillations in the myopic ant random walk on bipartite clusters[11,13] as well the as distinct transient regimes on close-packed lattices.[13] We have established this method as the basic generic method to compute almost any autocorrelation function very efficiently and thus allowing the comparison with other theoretical or numerical calculation of these functions. An example of such use is in the study of the effects of the anisotropy of the critical percolation cluster[14,15] where mean field calculations were compared with the *exact* ones computed by the enumeration method.

Two extensions of this method we made are (1) to include the persistence of the random walker (to account for the real time transport properties) and (2) to random walks with traps. The first extension will be discussed later in describing our work on frequency dependent conductivity in disordered networks. The second extension[16,17] is equivalent to the problem of so-called *ideal chain* where all trajectories of equal contour length are weighted equal, thus making contact with work on the polymer chain statistics in disordered media. In this project, we studied the conformational properties of the ideal chain for the first time in a critically disordered medium and contrasted the behavior with the corresponding one on some of the regular fractals.[17] For example, we have shown that the size $\langle R^2 \rangle$ does have a power-law dependence on the number of steps N (unlike on some regular fractals where the chain is *localized* by disorder) but the calculated Flory exponent ν is much larger than the anomalous diffusion exponent $1/d_w$. This result is interesting because it illustrates the role of *entropy trapping*, i.e., the fact that the highly connected regions of the medium contributes most of the statistical weight.

III. Langevin Analysis of Anomalous Diffusion

Third, an extension of the Langevin approach[18] to the dynamics of anomalous diffusion has been carried out.[19] Starting from the basic relation for the velocity autocorrelation function $C_v(t)$,

$$\frac{1}{2}\langle R(t)^2\rangle = t\int_0^t C_v(u)du - \int_0^t uC_v(u)du, \tag{2}$$

we can analyze what the leading behavior of $\langle R^2\rangle$ will be as a function of the long-time behavior of $C_v(t)$. For example, if $C_v(u) = o(u^{-2})$ (i.e., goes to zero faster than u^{-2}) and $\int_0^\infty C_v(u)du = D_\infty > 0$, then we have $\langle R^2\rangle \sim 2D_\infty t$. However, if C_v decays more slowly, additional possibilities arise. For example, if $C_v(u) \sim Au^{-x}$ with $1 < x < 2$ and $\int_0^\infty C_v(u)du = 0$, then we obtain both the cage effect, i.e., $A < 0$, and anomalous diffusion: $\langle R^2\rangle \sim t^{2-x}$. This result follows even when C_v is modulated by a more slowly decaying, oscillatory envelope.[11,19]

The question is how to modify the usual Langevin approach to render it consistent with such a slow decay of C_v. In this project, we have indicated a mean field approach in which the *effective* long-time correlation (due to spatial correlation in medium) is expressed by a time-dependent friction kernel $\alpha(t)$ in a generalized Langevin equation:

$$\frac{d}{dt}\mathbf{v}(t) = -\int_0^t \alpha(t-\tau)\mathbf{v}(\tau)d\tau + \frac{\mathbf{f}(t)}{m}. \tag{3}$$

From this, we obtain the first and second fluctuation-dissipation theorems, which specify the relationship between the velocity autocorrelation, random force autocorrelation, and the friction kernel. In the case of the critical percolation disorder, a single parameter, the decay exponent of the friction kernel, effectively replaces the fractal medium.

IV. Frequency Dependent Conductivity of Inhomogeneous Media

Fourth, we have combined the discrete-time discrete-space random walk with the linear response theory[20] to study the real, continuous time transport properties such as the frequency dependent electrical conductivity. This approach reproduces the Drude-like frequency dependence for homogeneous or ordered systems and in addition suggests various interesting possibilities for disordered mixtures depending on parameters such as the length-scale of disorder, the mean free path and the concentration of the charge carriers.

Within linear response theory, the conductivity $\sigma(\omega)$ at frequency ω is proportional

to the Laplace transform $\hat{C}_v(i\omega)$ of the velocity autocorrelation discussed above. Thus,

$$\sigma(\omega) \propto \hat{C}_v(i\omega) = -\frac{\omega^2}{2} \int_0^\infty \langle R(t)^2 \rangle e^{-\eta - i\omega t} dt \equiv D(\omega), \quad \text{as } \eta \to 0^+. \tag{4}$$

To relate the continuous time t to the number of hopping events we use the continuous-time random walk approach (CTRW).[21] The central concept in the CTRW is the waiting time distribution, which is the probability distribution for the time that a particle waits after one hop before attempting another hop. If there is no memory effect in the waiting time, the appropriate distribution is simply a Poisson distribution. We then represent the problem in terms of a discrete transition probability matrix $\mathbf{W}$. The use of this $\mathbf{W}$ then gives $D(\omega)$ in terms of the step autocorrelation of a discrete hop random walk:

$$D(\omega) = \frac{i\omega}{2} \frac{\hat{\psi}(i\omega)}{1 - \hat{\psi}(i\omega)} [\langle v(0)^2 \rangle + 2 \sum_{n=1}^\infty \langle \mathbf{v}(n) \cdot \mathbf{v}(0) \rangle \hat{\psi}(i\omega)^n], \tag{5}$$

where $-\psi(t)$ is the derivative of the waiting time distribution.

For no memory in waiting time, the first term is in fact independent of ω (giving the DC result), the only possible ω dependence coming from the second term. Such dependence may be due to the long-range spatial correlations in a disordered medium, or in a homogeneous (or ordered) medium, it may be due to the intrinsic correlation in the hopping events, e.g., the persistence in the direction of velocity. Indeed such a *persistent random walk* is needed to produce Drudelike ω dependence as the latter is the consequence of an exponential (and *not δ* function) decay in the velocity autocorrelation. This may be viewed as the result of a spatial coarse graining at the length scale a smaller than the mean free path l of the charge carrier. For our work, then, a is the lattice constant, and the important dimensionless parameter is the ratio $\eta = a/l$. For $\eta \gg 1$, the coarse-grained Brownian motion is clearly diffusive and the usual uncorrelated random walk will result, while for $\eta < 1$, there will be persistence effects.

We have constructed specific models of the persistent random walk whose diffusivity $D(\omega)$ in a homogeneous material can be cast in the Drudelike form and whose parameters can be completely determined by the physical parameters D (DC diffusivity), τ_{tr} (transport time), and the ratio η.[22] While $D(\omega)$ for such a model can be analytically evaluated for the homogeneous medium, a numerical evaluation becomes necessary if the medium is inhomogeneous. For this purpose, we have modeled the persistence by suitably enlarging the matrix $\mathbf{W}$ incorporating *internal states* (which describe how the particle has arrived at the present position). In a two- or multi-phase medium, we need to set the time scale for the hopping events using the maximum hopping rate in the whole sample as well as

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to define a suitable set of rules for scattering at the interfaces. The overall frequency dependent diffusivity is then calculated by first evaluating the step autocorrelation function by exact enumeration using **W** and then substituting the result in Eq.(5). Then the generalized Einstein relation gives the overall conductivity.

For the study of the effective conductivity of inhomogeneous media, it is often assumed that only the bulk conductivities of the individual phases are important and further that only the (transport) time scales control the latter. However, since

$$\sigma = \frac{ne^2}{k_B T} D \propto n l^2 \tau_{tr}^{-1} \ , \tag{6}$$

where n is the carrier density, these assumptions amount to neglecting the possible effects of the carrier concentration and mean free path. If the typical sizes of the domains of each phase are much larger than the mean free paths of the charge carriers, then the effective DC conductivity will indeed be independent of how the conductivity of each phase depends on n and l in the phase; however, this is not necessarily true for microscopic or mesoscopic disorder[23,24] and for the AC properties.

As an example, we exhibit the following special case in Fig.2. The diffusivities for the two phases A and B are equal and so are the transport times, but the carrier concentrations satisfy $n_A/n_B = 10^{-5}$, thus $\sigma_A/\sigma_B = 10^{-5}$. A site percolation realization is created with the fraction p_A of the poor phase on a square mesh of side $L = 100$ and an interface scattering rule is implemented such that a charge carrier is effectively trapped within the B phase with exit probability per step of $\sim n_A/n_B$. The particularly interesting case is when the persistence is very high, e.g., $\eta = 0.01$. Overall, the effective conductivity tends to remain flat until relatively high frequency, partly because the decoupling of the phases does not set in until such high frequencies because of the large mean free path. Also, at the percolation threshold for the good phase B ($p_A = 0.40$), there is a region where a fractal power law can be observed. However, the most noteworthy feature is that (1) for $p_A = 0.90$, i.e., mixing 10 % of good phase into the poor phase, the conductivity decreases, and (2) it remains lower than for $p_A = 1.00$ for even higher fraction of the B phase mixed in, at low frequencies. This can be interpreted ass the result of the drastic reduction in the effective mean free path because the good phase is spread into isolated *traps*. Clearly such effects could be seen only because the competition between the mean free path and the disorder length scale has been included in the calculation.

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Acknowledgments

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Figures

Fig. 1 Density $n(\lambda)$ of the eigenvalues for the transition probability matrix **W** of the blind ant problem on the square lattice percolation cluster with periodic boundary conditions. At $p = p_c \approx 0.593$, the scaling exponent is close to $d_s/2 - 1$, while it crosses over to a much flatter curve consistent with the exponent of zero.

Fig. 2 The real part of the frequency dependent diffusion conductivity for the highly persistent random walk model of a two phase random mixture. p_A is the fraction of the poor phase where $\sigma_A/\sigma_B = n_A/n_B = 10^{-5}$. The transport time and mobility in the two phases are taken equal.
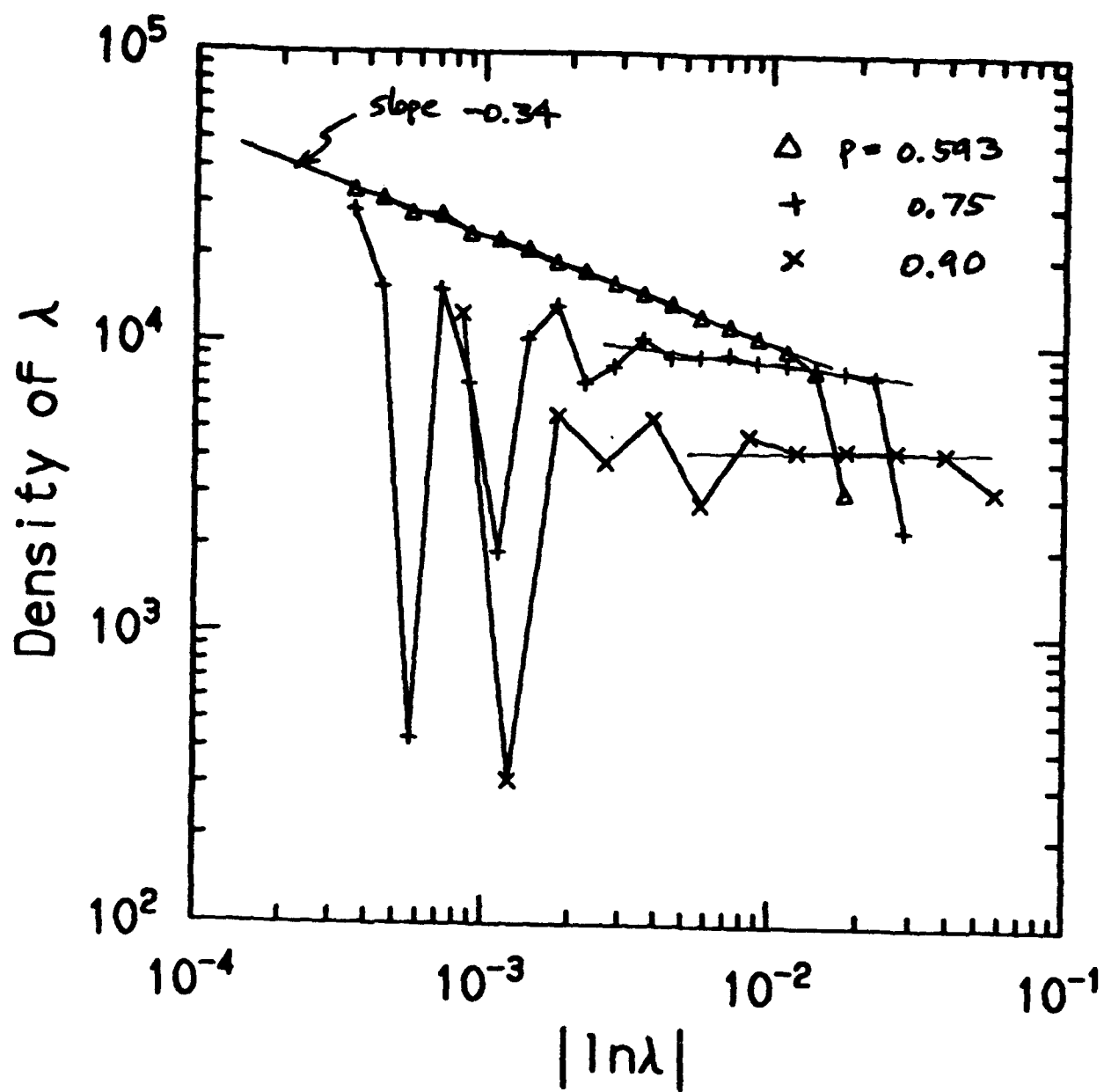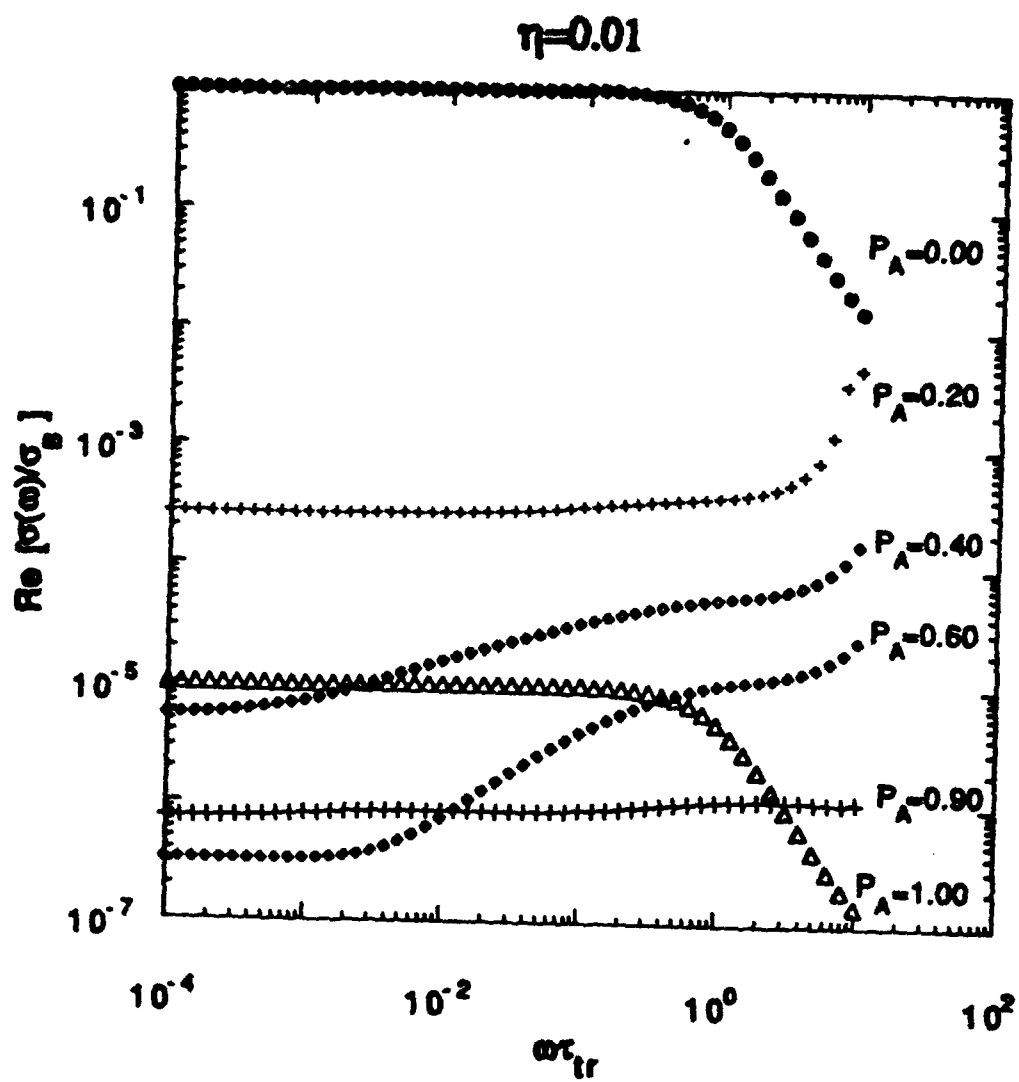
Fig. 1

$\eta = 0.01$

Re [$\sigma(\omega)/\sigma_B$]

$P_A = 0.00$

$P_A = 0.20$

$P_A = 0.40$

$P_A = 0.60$

$P_A = 0.90$

$P_A = 1.00$

$\omega\tau_{tr}$

Fig. 2

List of Publications Supported in Part by the ONR Grant

1. *Prewetting transition in supercritical Argon*
   (G. Ascarelli and H. Nakanishi), J. de Physique (Paris) **51**, 341–354 (1990).

2. *Auto-correlation functions for discrete random walks on disordered lattice*
   (D. Jacobs and H. Nakanishi), Phys. Rev. A **41**, 706–719 (1990).

3. *Scaling at the rod-to-flexible chain crossover in the stiff limit*
   (J. W. Halley, D. Atkatz, and H. Nakanishi), J. Phys. A **23**, 3297–3306 (1990).

4. *Anomalous diffusion: A dynamic perspective*
   (R. Muralidhar, D. Ramkrishna, H. Nakanishi, and D. Jacobs), Physica A **167**, 539–559 (1990).

5. *Self-avoiding Lévy walk: A model for very stiff polymers*
   (J. Moon and H. Nakanishi), Phys. Rev. A **42**, 3221 (1990).

6. *Eigenvalue spectrum of hopping transport on critical percolation clusters*
   (N. H. Fuchs and H. Nakanishi), Phys. Rev. A **43**, 1721–1726 (1991).

7. *Exact enumeration study of self-avoiding walks on two-dimensional percolation clusters*
   (H. Nakanishi and S. B. Lee), J. Phys. A **24**, 1355–1361 (1991).

8. *Diffusion on two-dimensional percolation clusters: Influence of cluster anisotropy*
   (R. Muralidhar, D. Jacobs, D. Ramkrishna and H. Nakanishi), Phys. Rev. A **43**, 6503–6517 (1991).

9. *Onset of excluded-volume effect for the statistics of stiff chains*
   (Jangnyeol Moon and Hisao Nakanishi), Phys. Rev. A **44**, 6427–6442 (1991).

10. *Ideal Chain on Two-Dimensional Critical Percolation Cluster*
   (A. Giacometti, H. Nakanishi, A. Maritan and N. H. Fuchs), J. Phys. A (1992), in press.

11. *Anomalous Diffusion in Disordered Clusters* in *On Clusters and Clustering: From Atoms to Fractals*, ed. P. J. Reynolds, North-Holland (1992), in press.

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12. *A Precise Determination of the Backbone Fractal Dimension on Two-Dimensional Percolation Clusters*
    (M. D. Rintoul and H. Nakanishi), J. Phys. A (submitted).

13. *Self-Avoiding Walk on Critical Percolation Cluster*
    (H. Nakanishi and J. Moon), Physica A (submitted as contribution to the International Conference on *Fractals and Disordered Systems*, to be held in July, 1992 in Hamburg, Germany).

14. *Random Walks on Random Systems: Eigenspectrum of Large Markov Matrices*
    (H. Nakanishi, S. Mukherjee and N. H. Fuchs), preprint.